AD-A267 573

NTATION PAGE

Form Approved
OMB No. 0704-0188

ORT DATE	3. REPORT TYPE AND DATES COVERED
7/93	TECHNICAL

4. TITLE AND SUBTITLE
PHOTOCHEMICAL STUDIES OF THE EASTERN CARIBBEAN: AN INTRODUCTORY OVERVIEW

5. FUNDING NUMBERS
ONR N00014-85-C-0001
ONR N00014-87-K-0007
ONR N00014-89-J-1258
NSF OCE84-17770
OCE87-00576, OCE91-15608

6. AUTHOR(S)
ROD. G. ZIKA, PETER J. MILNE AND OLIVER C. ZAFIRIOU

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
WOODS HOLE OCEANOGRAPHIC INSTITUTION
WOODS HOLE, MA 02543

8. PERFORMING ORGANIZATION REPORT NUMBER
WHOI CONTR. NONE

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
OFFICE OF NAVAL RESEARCH
ENVIRONMENTAL SCIENCES DIRECTORATE
ARLINGTON, VA 22217-5660

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
In citing this report in a bibliography, the reference given should be:
JOURNAL OF GEOPHYSICAL RESEARCH 98(C2):2223-2232, 1993

12a. DISTRIBUTION/AVAILABILITY STATEMENT
APPROVED FOR PUBLIC RELEASE:
DISTRIBUTION UNLIMITED

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

This special section of the Journal of Geophysical Research reports a multi-investigator study of a number of sunlight-initiated photoprocesses taking place in the varied biogeochemical and oceanographic environment found in the tropical Eastern Caribbean and Orinoco River delta in the spring and fall of 1988. Principal conceptual themes that were addressed by the program included (1) the characterization of the role of dissolved organic matter as the main chromophore initiating photoprocesses in surface seawater, (2) the determination of the fluxes and pathways of reactants and transient species involved in oxygen photoredox chemistry, and (3) the continuing development of chemical mapping strategies, including observing and modelling reactive phototransient distribution in terms of their sources, mixing, and fates. Ancillary supporting studies included observation of water mass tracers, dissolved trace gases, atmospheric components, nutrients and the geochemistry of estuarine mixing processes in an important continental margin. The observational and mechanistic investigations reported here feature a number of novel or improved methods allied with some advanced underway sampling, sensing and computing facilities that were implemented aboard the R/V *Columbus Iselin*. Results from the study showed large-scale (~1000 km) seasonal variations in surface water photoreactivity, optical and biooptical characteristics over much of the Caribbean basin. These changes resulted from seasonally varying riverine inputs of organic chromophores, nutrients and suspended material. Smaller scale (10-100 km) studies carried out in the Orinoco delta and the Gulf of Paria showed that estuarine mixing processes did not affect major net removal of dissolved organic matter, consistent with the hypothesis that riverine chromophore input plays a dominant role in open-water photochemistry.

14. SUBJECT TERMS
1) PHOTOCHEMISTRY
2) EASTERN CARIBBEAN
3) INTRODUCTION

15. NUMBER OF PAGES
10

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 98, NO. C2, PAGES 2223–2232, FEBRUARY 15, 1993

Photochemical Studies of the Eastern Caribbean: An Introductory Overview

ROD G. ZIKA AND PETER J. MILNE
Rosenstiel School of Marine and Atmospheric Science, University of Miami, Florida

OLIVER C. ZAFIRIOU
Woods Hole Oceanographic Institution, Woods Hole, Massachusetts

This special section of the Journal of Geophysical Research reports a multi-investigator study of a number of sunlight-initiated photoprocesses taking place in the varied biogeochemical and oceanographic environment found in the tropical Eastern Caribbean and Orinoco River delta in the spring and fall of 1988. Principal conceptual themes that were addressed by the program included (1) the characterization of the role of dissolved organic matter as the main chromophore initiating photoprocesses in surface seawater, (2) the determination of the fluxes and pathways of reactants and transient species involved in oxygen photoredox chemistry, and (3) the continuing development of chemical mapping strategies, including observing and modelling reactive phototransient distribution in terms of their sources, mixing, and fates. Ancillary supporting studies included observation of water mass tracers, dissolved trace gases, atmospheric components, nutrients and the geochemistry of estuarine mixing processes in an important continental margin. The observational and mechanistic investigations reported here feature a number of novel or improved methods allied with some advanced underway sampling, sensing and computing facilities that were implemented aboard the *R/V Columbus Iselin*. Results from the study showed large-scale (~1000 km) seasonal variations in surface water photoreactivity, optical and biooptical characteristics over much of the Caribbean basin. These changes resulted from seasonally varying riverine inputs of organic chromophores, nutrients and suspended material. Smaller scale (10-100 km) studies carried out in the Orinoco delta and the Gulf of Paria showed that estuarine mixing processes did not affect major net removal of dissolved organic matter, consistent with the hypothesis that riverine chromophore input plays a dominant role in open-water photochemistry.

1. OBJECTIVES

Historically, the study of light in the oceans has revolved primarily around two themes: the role light plays in animal ecology and its key control of primary production. A third dimension, namely, the photochemical interaction of sunlight with seawater constituents and the resulting environmental consequences, has joined these traditional themes. In the 1970's these processes were usually studied in the laboratory; by the 1980's they had advanced to specific process measurements at sea and real-time surveys of photochemically derived reactive transient species. Currently, investigations in marine photochemistry include (1) examination of the nature and reactivity of the chromophores found in the dissolved organic matter in seawater, (2) the penetration of sunlight and especially UV-B radiation in the surface ocean, (3) the remote sensing of pigment and chromophore concentrations, (4) the photoredox chemistry of transition metals and metal-organic complexes, (5) the production of free radical species by sunlight (e.g. radicals associated with H_2O_2, namely, OH, O_2^-, HOO), and (6) the relative importance of inputs of terrestrial organic matter to the marine organic carbon pool and the subsequent rate of its remineralization [*Miller*, 1983; *Zafiriou* 1983; *Zafiriou et al.*, 1984; *Newman*, 1984; *Zika*, 1987; *Zika and Cooper*, 1987; *Blough and Zepp*, 1990].

In 1986 these expanded capabilities coalesced with a new understanding of the very large-scale effects of riverine inputs on the central Caribbean, as revealed by the ^{226}Ra studies and model of *Moore et al.* [1986]. It became clear that basinwide effects of riverine input, as evidence by salinity, silicate [*Froehlich et al.*, *1978*], and ^{228}Ra signatures, might imply a corresponding basin-scale terrestrial influence on surface water photochemistry driven by this riverine input of photoreactive dissolved organic matter (DOM). This special section reports the results of two multi-investigator cruises, undertaken in spring and fall, 1988 in the eastern Caribbean, Gulf of Paria, and Orinoco delta regions (see Figure 1 and Table 1 for locations) to pursue this hypothesis. While previous photochemical work has shown that riverine inputs render some smaller, restricted coastal water bodies highly photoreactive (e.g. Whitewater Bay, at the mouth of the Florida Everglades [see *Moffet and Zika*, 1987]), it was uncertain whether or not this conclusion was extendable to basin-scale systems. Several reports have suggested that estuarine removal processes may prevent substantial amounts of riverine DOM components from reaching the open sea [*Sholkovitz, 1976; Sholkovitz et al., 1978*], thus minimizing their participation in photochemical reactions on larger scales.

Hence, some key questions addressed in this program were as follows.

1. Can large-scale riverine influx affect photochemistry on a basin-size scale?

2. To what extent does seasonal variation of the Orinoco River plume influence optical and photochemical properties of the eastern Caribbean?

3. Can existing optical and photochemical measurement capabilities be used to synoptically describe larger scale chemical distributions?

This paper presents a necessarily cursory introduction to the oceanographic features of the study area, describes some common shipboard instruments and sampling techniques that are referred to in several of the papers, and briefly recapitulates the individual studies and major findings from these cruises.

Paper number 92JC02759.
0148-0227/93/92JC02759$05.00

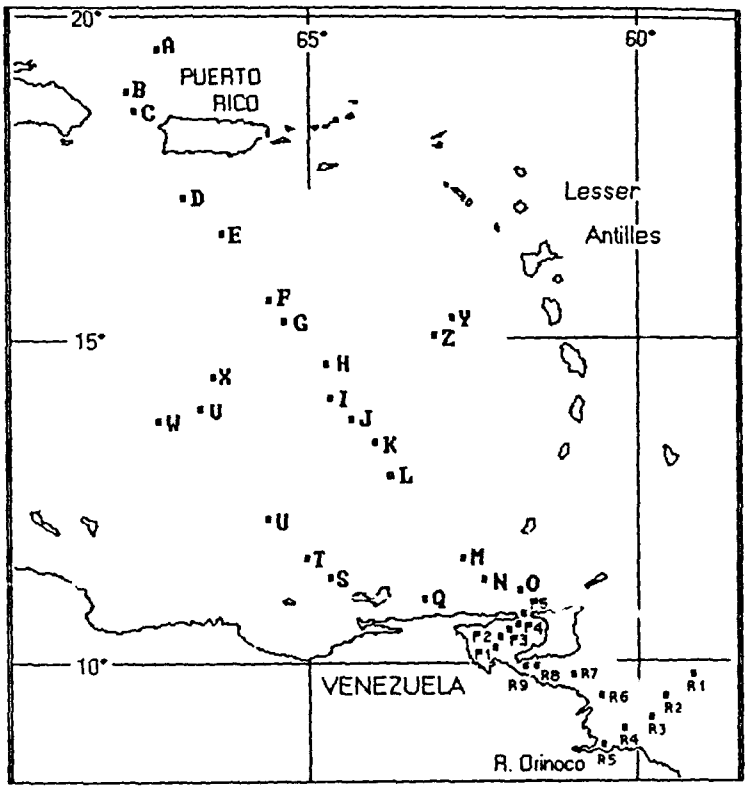

Fig. 1. Study area and station locations (see also Table I).

2. THE EASTERN CARIBBEAN

This sea is semi-enclosed by continental land masses and separated from the adjacent Atlantic ocean by a high sill associated with the Antilles arc. Bottom water in the Caribbean Sea enters over the sills in the region of the Anegada Passage to the east of Puerto Rico [*Dietrich*, 1937; *Wust*, 1963; *Worthington*, 1971; *Sturges*, 1970]. Quantitative details of the size of the renewal flows and their frequency are incompletely known [*Kinder et al.*, 1985]. In the warm surface ocean, westward advection of northern tropical Atlantic waters through the Lesser Antilles arc is dominant [*Morrison and Nowlin*, 1982; *Heburn and Rhodes*, 1987]. Again, the relative flows through the major passages are not as well constrained as the net outflow from the Caribbean, which has been determined by long term transport measurements made in the Straits of Florida [*Molinari et al*, 1985]. For example, the relative contribution of North Atlantic water entering through the Windward Passage (between Cuba and Hispaniola) and water entering through the southern Lesser Antilles remains uncertain [*Mazeika et al.*, 1980; *Stalcup and Metcalf*, 1972; *Nof and Olson*, 1983; *Kinder et al.*, 1985]. In the surface layers, tidal and current meter records, drifter buoys, and hydrographic data have been used to assess the spatial and temporal flow variability. Mesoscale eddies and meanders have been observed, especially in the northern Caribbean [*Molinari et al.*, 1979]. Earlier inferences of a weak eastward flowing countercurrent have not been substantiated from coastal zone color scanner (CZCS) imagery [*Muller-Karger et al.*, 1989], the suggestion being that these observations were based on incomplete sampling of mesoscale features [*Kinder et al.*, 1985].

Between January and April, the Intertropical Convergence Zone (ITCZ) resides at its southernmost position near the equator. From May through August the ITCZ moves to 6-10° N where it may induce an eastward flowing North Equatorial Counter Current [*Busalacchi and Picaut*, 1983; *Richardson and McKee*, 1984]. Water from the retroflected North Brazil Current [*Johns et al.*, 1990] and water from the Amazon River outflow may combine with this eastward flowing current [*Muller-Karger et al.*, 1988], dispersing the summer flood plume of the Amazon out into the Atlantic. The degree to which northward flowing Amazon outflow joins with the coastal flow of the Orinoco plume and enters the southern Caribbean remains unclear.

This seasonality of the position of the ITCZ corresponds to the dry (February-May) and wet (August-October) seasons [*Etter et al.*, 1987]. The accompanying seasonal variation of the runoff of the three large rivers that influence the Caribbean, namely, the Amazon, the Orinoco, and the Magdalena, dominates the surface salinity patterns of the region. These rivers together contribute about 20% of the total fresh water discharge to the world's oceans. In particular, the Orinoco is the world's third largest non-tributary river by discharge (36,000 $m^3 s^{-1}$ [*Lewis and Saunders*, 1989]). Because the river is hydrologically unregulated and has a minimally disturbed watershed, its weighted mean discharge of both suspended (80 mg L^{-1}; or 90 x 10^6 t yr^{-1}) and dissolved (34 mg L^{-1}) substances is high. Estimates of both the transport of organic carbon (6.8 x 10^6 t yr^{-1}, approx 1.6% of global river transport) and total nitrogen (0.54 x 10^6 t yr^{-1}, approx. 1.5% of global river transport) have been made [*Lewis and Saunders*, 1989] attesting to the influence of the Orinoco's flow on the chemistry of the Caribbean.

TABLE I. Positions of Station Locations on Orinoco Cruises 1988

Station	Position		Spring	Fall
A	19°25.1N	67°24.9W	-	x
B	18 54.2	67 46.9	x	-
C	18 37.6	67 38.7	x	-
D	17 17.5	66 53.2	x	x
E	16 39.2	66 20.5	x	-
F	15 40.7	65 32.5	x	-
G	15 20.1	65 18.0	x	x
H	14 40.6	64 45.8	x	x
I	14 11.3	64 40.5	x	-
J	13 45.0	64 24.6	x	-
K	13 29.6	64 04.3	x	-
L	12 54.4	63 45.0	x	x
M	11 48.1	62 45.4	x	x
O	11 05.2	61 59.7	-	x
P1	10 15.2	62 10.1	x	x
P2	10 22.0	62 09.5	-	x
P3	10 29.6	61 59.9	x	x
P4	10 36.4	61 53.6	-	x
P5	10 44.4	61 48.1	x	-
Q	10 57.6	63 18.4	-	x
R1	09 50.4	59 09.7	x	x
R2	09 31.7	59 31.5	x	x
R3	09 10.8	59 50.2	x	x
R4	08 58.6	60 10.3	x	x
R5	08 37.3	60 29.8	x	x
R6	09 30.7	60 36.1	x	x
R7	09 50.4	61 02.1	x	x
R8	09 55.2	61 34.9	x	-
R9	09 56.7	61 37.6	x	-
S	11 22.3	64 46.8	x	-
T	11 39.5	64 59.3	x	-
U	12 20.1	65 39.8	x	-
V	14 00.0	66 39.4	x	-
W	13 51.1	66 39.4	x	-
X	14 24.3	66 31.5	-	x
Y	15 20.7	62 48.7	x	x
Z	15 12.9	63 08.1	-	x

In subsequent papers of this section, stations are designated by a letter followed by /F or /S for Fall or Spring cruise with an extension number if occupied more than once on that cruise. Orinoco River coastal stations are labelled R1 to R9, and stations in the Gulf of Paria are labelled P1 to P5.

Based on detailed consideration of CZCS imagery of chlorophyll pigments from 1979-1983, *Muller-Karger et al.* [1989] have revised the assumption that the Amazon is the dominant freshwater source into the Caribbean, arguing instead that it is the Orinoco plume, and to a lesser extent the effect of the Magdalena River, that are most important. Remotely sensed images of phytopigments resulting from the Orinoco plume showed the large areal coverage (> 3 x 10^5 km^2 [*Muller-Karger et al.*, 1989] of the plume in the Caribbean basin. In addition to CZCS images, chemical information has been used to study the dispersion of the Orinoco River plume in the eastern Caribbean. Measurements of dissolved silicate [*Froehlich et al.*, 1978] correlated well with the seasonal salinity fluctuations observed in the fall of each year; however, it was argued that the Amazon was the principal source of this high silicate freshwater influx.

Data presented in papers in this special section show that photochemical measurements can also differentiate the riverine plume. For example, (Figure 2*a*), the fluorescence signal of the DOM is clearly visible in the transect W-Y (see Figure *1*) taken in the central Caribbean during the fall cruise [see *Moore et al*, this issue]. These DOM fluorescence measurements do not necessarily allow a distinction between Orinoco and Amazon water, which may admix near the Orinoco River mouth [see *Moore and Todd*, this issue]. The westward dispersion of DOM fluorescence is consistent with the prevailing currents. Figure 2*b* shows a related photochemically derived parameter, hydrogen peroxide concentration (for details, see *Moore et al.* [this issue]). The interpretation of the H_2O_2 sections is made more complex by the diurnal variation associated with its photoproduction in surface waters [see *Sikorski and Zika*, this issue]. Related optical

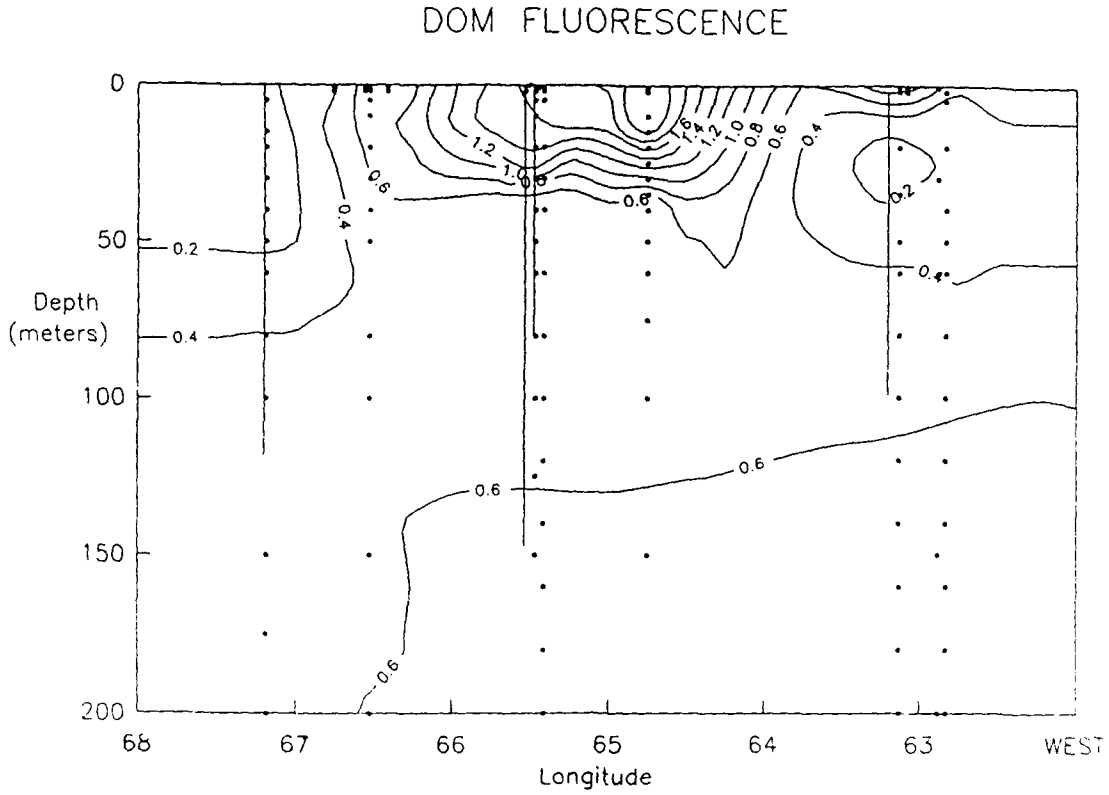

Fig. 2*a*. East-west transect across stations W-Y, fall, 1988. Plot shows contoured section of dissolved organic matter (DOM) fluorescence.

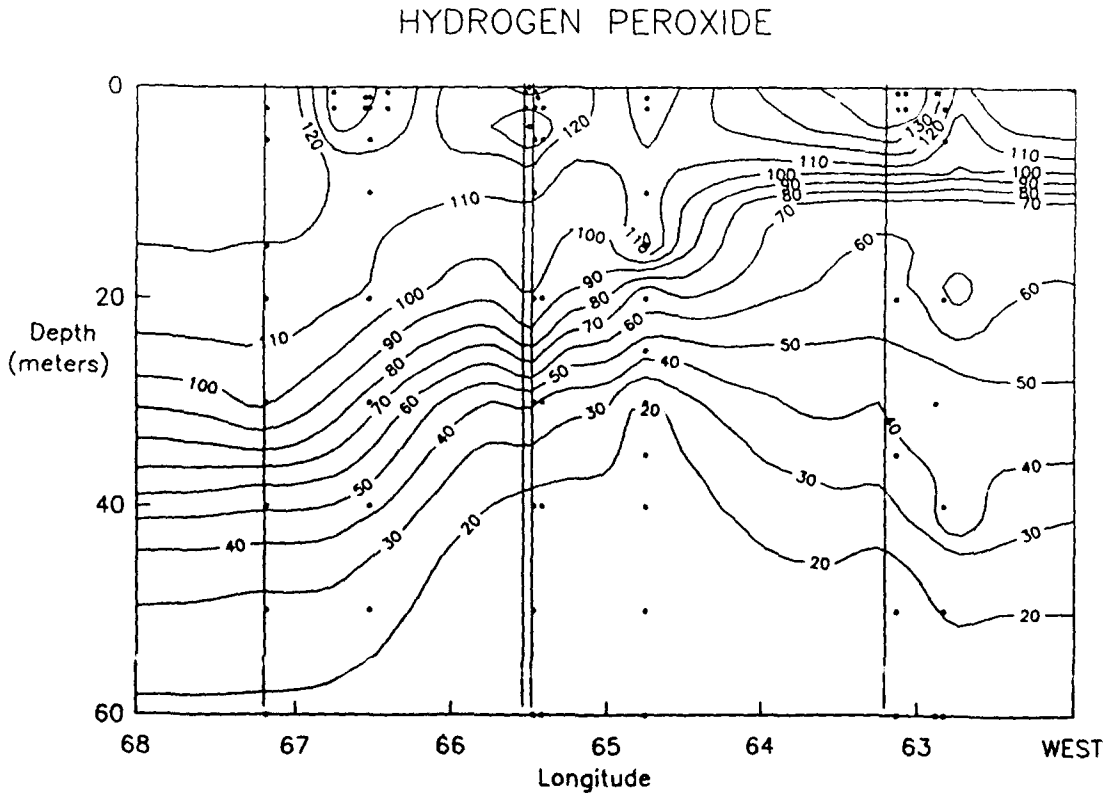

Fig. 2*b*. East-west transects across stations W-Y, fall, 1988. Plot shows contoured section of hydrogen peroxide concentration.

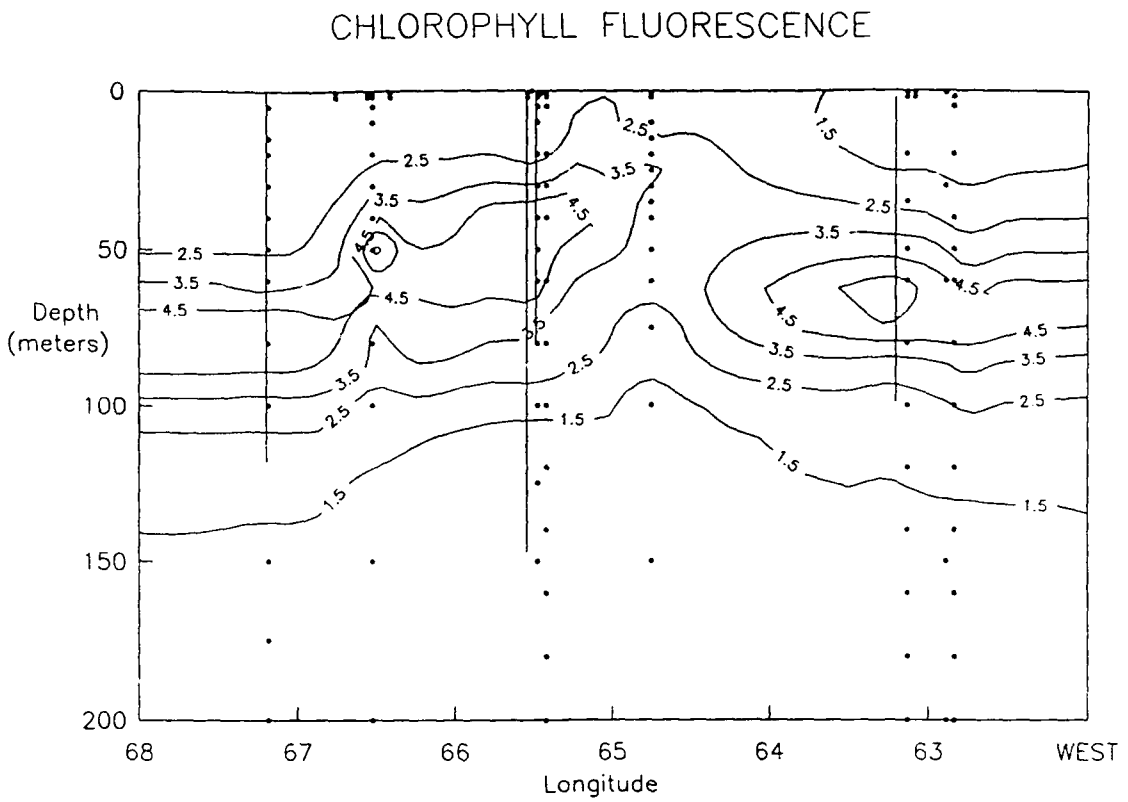

Fig. 3*a*. East-west transects across stations W-Y, fall, 1988. Plot shows contoured section of chlorophyll *a* fluorescence.

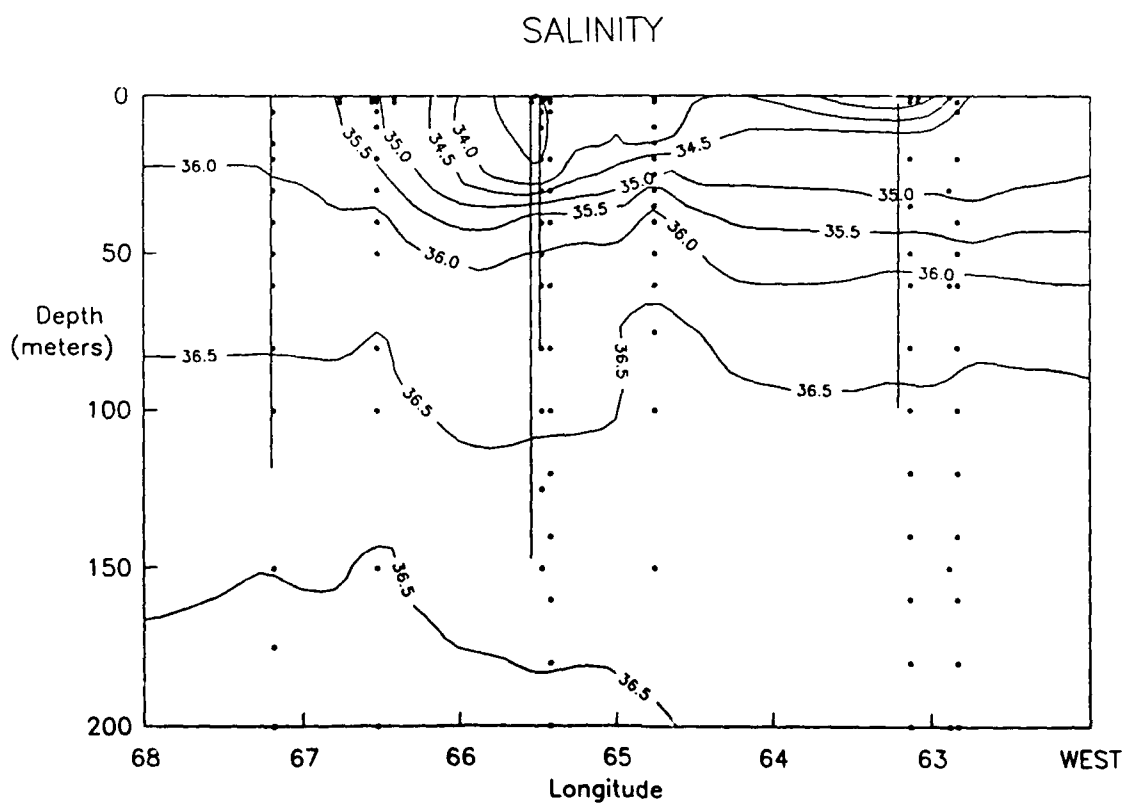

Fig. 3*b*. East-west transects across Stations W-Y, fall, 1988. Plot shows contoured section of salinity.

parameters (spectrally resolved underwater irradiance profiles and absorption coefficients) were also obtained for this transect [*Farmer et al*, this issue]. These data sets aid in the delineation of the riverine plume in conjunction with the more conventional oceanographic parameters of chlorophyll a fluorescence (Figure *3a*) or salinity (Figure *3b*).

3. SHIPBOARD FACILITIES FOR PHOTOCHEMICAL STUDIES

The demands for continuous and underway sampling and for better resolved monitoring have spurred the development of several novel "at-sea" analytical capabilities. The Miami group has made a number of modifications to the sea-going capabilities of the University of Miami's research ship, R/V *Columbus Iselin*, for shared use in photochemical studies, described here to avoid duplication in the subsequent papers.

Ship computer facilities. Two networked DEC microVAX 3 computers (Digital Equipment Co., Maynard, Massachusetts) handled data collection and processing and provided real-time display of on-line environmental parameters. An automatic data logging system (CIDS or Centralized Integrated Data System [*Samuels, 1988*] incorporated part of the older SAIL (Serial ASCII Instrumentation Loop) system. Continuously logged measurements included wet and dry bulb temperatures, barometric pressure, wind speed and direction, integrated solar irradiance, sea surface temperature and salinity. Ship position, heading, and speed were also logged. CIDS also logged data from a Doppler Current Profiler (RD Instruments, San Diego, California), through a DEC VAX/VMS DOS virtual disk service. Calibration and correction files were generated and stored for post processing of the data.

A user interface, which permitted the addition of other PC-DOS compatible computers to the system, provided additional data acquisition and handling capabilities and tape back-up of independent computer systems. Data could also be further tabulated and downloaded in standard ASCII format to PC-DOS compatible diskettes.

Bow sampling system. Clean seawater was delivered to both the wet and dry laboratories by a "through-the-hull" sampling system. The bow probe was located at approximately 2-m depth, near the bow. To avoid contamination of the sampled water, filters or screening mesh were not used. A positive displacement pump with an inert head (chlorosulfonated polyethylene, Hypalon^R from DuPont Co, Wilmington, Delaware), was mounted below the water line in the bow lazarette. This pump distributed the water through an all-Teflon (3/4 inch OD) pipe system to five outlets in the labs. The flow rate through the ship was 3-5 L min^{-1}, with a residence time in the system of less than 10 s. Individual teflon needle valves allowed researchers to control flow rate and delivery independently to their instrumentation. The system's high flow rate and an open down-fall provided a constant residence time for the water, independent of use.

Comparisons of chemical analyses (DOM fluorescence, absorbance, hydrogen peroxide, and nutrients) between water sampled from the flow system, bucket samples and "just-under-the-surface" Niskin bottle samples demonstrated that the flow system provided representative samples of the surface water.

Vertical integrating pumping system (VIPS). To obtain continuous underway (3 knots or 1.54 m s^{-1}) depth integrated profiles of conductivity, temperature, hydrogen peroxide, DOM and chlorophyll fluorescence, a submersible pumping system was developed. A submersible motor (Franklin Electric, Bluffton, Indiana) drove a magnetically coupled gear pump (Tuthill Corp, Chicago, Illinois) fitted with a Hastaloy pump head and teflon intake and output lines. The system incorporated a CTD (model 513E CTD, InterOcean Inc., San Diego, California) and an onboard computer (Onset Computer Co., N. Falmouth, Massachusetts) for A/D conversions. These components were enclosed in an epoxy coated aluminum cage approximately 1 m in diameter and 1.5 m high.

The VIPS cable (South Bay Cable Division, Consolidated Products Corp., Idyllwild, California) was constructed around nylon tubing (0.95 cm - 3/8 inch ID) that served to transfer the seawater from the pump head to an all-Teflon distribution system aboard ship. Surrounding the nylon tubing were 20 single electrical conductors for power and communications. The conductors were in turn sheathed by two Kevlar strength member layers, and the entire cable bundle was surrounded by a polyurethane plastic jacket. The cable was 2.46 cm thick, had a minimum bend diameter of 96 cm and a maximum working load of 1800 kg.

A large winch and block were required as a result of the large minimum bend radius of the cable. Precise winch control was achieved through special gearing and an hydraulic drive control. The winch was equipped with an electrical slip ring unit combined with a non-contaminating fluid swivel assembly (Nova Scotia Research, Dartmouth, Nova Scotia) which allowed the nylon tubing in the cable to be attached to a teflon tubing transfer line to the labs. An awning over the winch shaded the cable from direct sunlight, reducing temperature changes in water samples.

The VIPS was launched and recovered with the winch under the control of the deck crew or from the laboratory. Wire angle and winch status were continuously monitored with two video cameras. A PC-DOS computer program was written to display real-time salinity, temperature and depth data from the CTD and near real-time profiles of hydrogen peroxide, chlorophyll and DOM fluorescence. It took approximately 11 min for water to reach the analytical instruments, from the pump, which delivered approximately 4 L min^{-1} of seawater to the laboratory.

A descent rate of approximately 5 m per minute was found to produce the most detailed profiles. When vertical speed exceeded 10 m per minute, fine structure of the water column was lost. This was in part due to mixing of the water within the 300 m of sample tubing and partly due to smaller sample volume at each depth. Slower vertical speeds affected mixing within the cable less. Injections of dilute H_2O_2 stock solutions in the pump intake for an approximately 10 s duration produced symmetrically shaped clean peaks with a half-width of 1-2 min, after passing through the pump, 300 m of tubing, and another 20 m of teflon tubing in the distribution system.

It was previously determined that the metal surfaces of the pump head slightly increased the concentration of hydrogen peroxide. This production was quantified and subtracted from all the reported H_2O_2 data, as a simple offset. The value and form of the correction factor was determined by comparison between profiles produced with a calibration based on standard additions to surface water, to those calibrated at the bottom of a hydrocast (>150 m) where the initial concentration of H_2O_2 could be assumed to be zero (± the precision of the analytical method). This assumption was verified by batch peroxide determinations on water samples from associated hydrocasts. The offset was found to be approximately 30 nM and had no significant pressure/depth or time dependence within the upper 200 m of the water column. No artifacts were detected for fluorescence or absorbance signals when comparisons were made between "bucket" samples, Niskin water bottles, the bow pumping system and the VIPS system sampling at the same depth.

During the Orinoco cruises, chlorophyll fluorescence and DOM fluorescence were measured using on-line fluorometers (Model 10, Turner Designs Inc, Sunnyvale California) equipped with flow cells. The instrumental conditions used excitation wavelength 430 nm, emission wavelength > 650 nm for chlorophyll a fluorescence and excitation wavelength 350 nm, emission wavelength 496 nm for DOM fluorescence. Hydrogen peroxide was measured with the modified scopoletin-HRP method [*Zika and Saltzmann*, 1982] in a flow injection mode using a filter fluorometer (model FD-100, SpectroVision Inc, Chelmsford, Massachusetts) as a detector. The fluorometer filters used were excitation 365 nm, emission 496 nm. The distribution lines inside the ship paralleled the bow-sampling system described above, and the feed system to the instruments were valve selectable for either the VIPS cast or continuous surface seawater.

One advantage of using the VIPS was the ability to obtain continuous profiles. Hydrogen peroxide, chlorophyll fluorescence and DOM fluorescence data from a VIPS cast are presented, and compared to the CTD cast for the same station, in Figure *4*. The DOM profile (Figure *4c*), showed the elevated fluorescence of the Orinoco River water overlying oligotrophic seawater in the photic zone. Details of the analytical methods and discussion of the data are given in *Moore et al.* [this issue]. This increased resolution provided by the VIPS is important to the understanding of the distribution of chemical compounds in the surface ocean and is especially desirable for the validation of mixed layer models. Dynamic changes in the water column can be easily observed with repetitive VIPS casts, without great delay for recovering instrumentation, and with lower risk of contamination. It also permits repetitive sampling at selected depths in almost real time. Integrated samples through the water column and larger volume samples are also easily obtained.

Spectral irradiance and solar insolation. A shipboard solar radiometer and integrator (model PSP precision pyranometer, 285 - 1100 nm spectral range, Eppley Lab Inc, Newport, Rhode Island) was used to continuously monitor incident solar radiation during the two cruises. The shipboard data logging system recorded both the instantaneous measurement and cumulative integrated irradiance. Spectrally resolved irradiance, both in air and underwater, were measured using two underwater spectroradiometers (LI-1800UV, Li-Cor Inc, Lincoln, Nebraska). The deck mounted spectroradiometer was used to record wavelength specific information for deck irradiation experiments. It also provided a reference for total incident sunlight when underwater irradiance measurements were being made. The second spectroradiometer was mounted in a submersible instrument package together with a pressure sensor for precise depth determination (InterOcean Inc, San Diego, California). The underwater radiometer was positioned at known depths off the port side of the ship to measure *in situ* light levels in the upper water column. A more detailed discussion of the use of the Li-Cor radiometers and how the data was processed is discussed by *Farmer et al.* [this issue].

4. OVERVIEW OF SPECIFIC STUDIES

A range of optical, photochemical and geochemical studies are presented in this special section. Two papers concern the effects the Orinoco plume on the primary productivity of the Eastern Caribbean. *Bonilla et al.* [this issue] measured dissolved nitrogen, silicate and primary productivity to assess the fate of river-borne nutrients and their impact on the productivity of Caribbean waters. *Bidigare et al.* [this issue] used HPLC measurements of photosynthetic pigments to contrast changes in phytoplankton

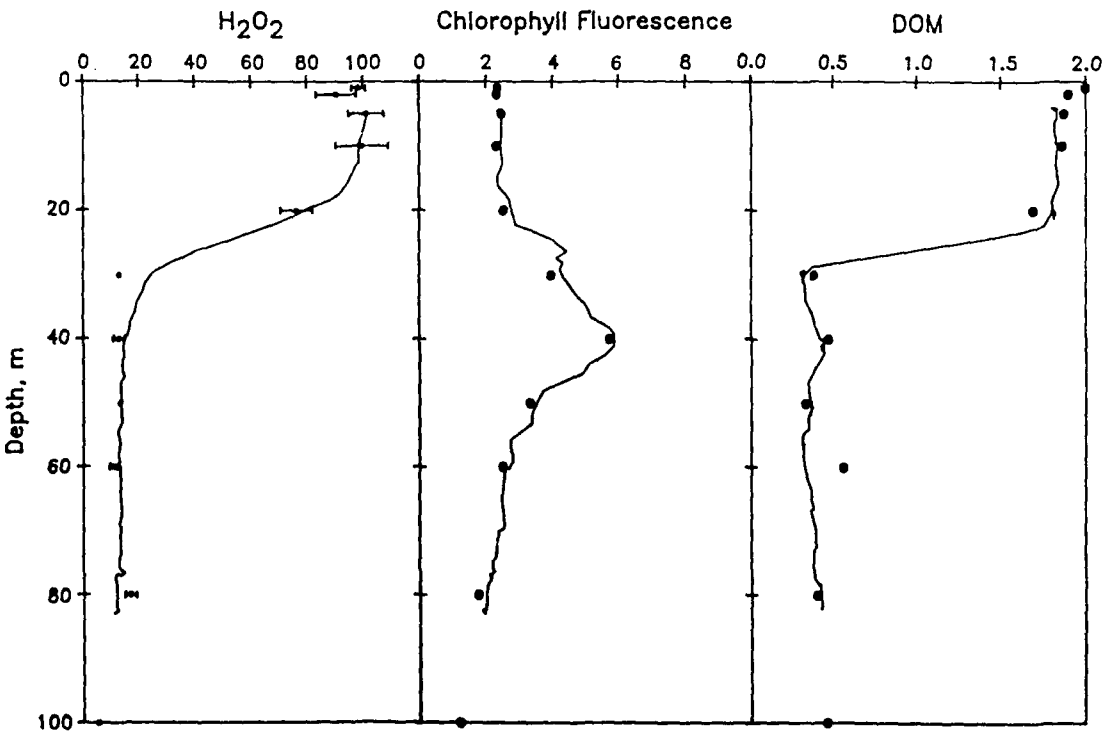

Fig. 4. Comparison of vertically integrated profiler (continuous lines) with rosette CTD hydrocasts (discrete points) at one station for chemical parameters (station G, fall, 1988): (*a*) hydrogen peroxide, (*b*) chlorophyll *a* fluorescence, (*c*) DOM fluorescence (in quinine sulfate units) [see *Moore et al.*, this issue].

species induced by the surface turbidity associated with the Orinoco plume. They demonstrated differences in the photoadaptive state of plankton, induced by the seasonally elevated attenuation coefficients in the water column. An *in situ* data set collected by *Farmer et al.* [this issue] consists of spectrally resolved underwater irradiance measurements on both the spring and fall cruises. The data set shows especially the extent to which the Orinoco plume alters the underwater light field throughout the region. The underwater light field in part determines the growth of the phytoplankton which produce the deep chlorophyll maximum.

Optical characterization of DOM carried into the Caribbean by the Orinoco [*Blough et al*, this issue], by both direct measurement of seawater samples and also of DOM extracts [*Amador et al.*, 1990], represents an important data set for the optical characterization of Type II and III waters. Specific absorption coefficients of Orinoco DOM are tabulated and the effect of estuarine mixing on the transport of DOM is discussed. Such measurements will be needed for the quantitative extension of remotely sensed ocean color imagery [e.g., *Muller-Karger et al.*, 1988, 1989] into coastal water regimes. The absorption properties of the chromophores in seawater are also crucial to the description of the photochemical properties and fates of these materials.

Two papers are concerned with the photochemical generation of free radical species as influenced by both the constituents of the Orinoco plume and the background chemical composition of the eastern Caribbean. *Dister and Zafiriou* [this issue] extend their "NO-scavengeable" measurement of free radical production rates, documenting large-scale areal and seasonal trends in this parameter for this unique water mass regime. In the Orinoco River estuary proper, very high radical production rates were encountered; the implications of these measurements are discussed. *Micinski et al* [this issue] were concerned with the photochemical production of one key free radical species, namely the superoxide anion. Using a chemical trapping technique involving isotopically labelled substrates, these authors suggest that the superoxide radical is quantitatively the dominant reactive transient species produced in the photochemical irradiation of seawater.

The dismutation of the superoxide radical results in the production of the major photoproduct hydrogen peroxide, which serves as a focus for a number of studies presented here. Hydrogen peroxide appears to be the dominant photoredox mediator in seawater. It warrants attention because of the impact it may have on the chemical speciation of other constituents in the water column. Measurements of the production rate and also the distribution of H_2O_2 in the eastern Caribbean and how these are altered by the presence of the Orinoco plume are detailed by *Moore et al.* [this issue]. Using an isotopic labelling technique, *Moffet and Zafiriou* [this issue] have made measurements of the photochemical degradation rate of H_2O_2, a major decomposition pathway for this photoproduct.

Another metastable product of photochemistry is carbon monoxide, CO. *Jones and Amador* [this issue] report on the distribution of carbon monoxide and methane throughout the region. Carbon monoxide, along with a number of other low molecular weight carbon compounds, is likely to be produced abiotically in surface seawater by the photooxidation of dissolved organic material [*Wilson et al*, 1970; *Conrad and Seiler*, 1980; *Redden* 1983]. These authors also consider consumption processes, in particular the microbial oxidation of CO, which is necessary to clearly understand the observed distribution of a photochemical product in seawater. The photochemical degradation of dissolved organic carbon in surface ocean waters has recently been suggested as being a quantitatively important process in understanding carbon cycling [*Kieber et al.*, 1989; *Mopper et al.*, 1991). Atmospheric measurements of carbonyl compounds by Zhou and Mopper considers photochemical modifications of marine derived organic material taking place in the marine boundary layer.

Waite and Szymczak [this issue (*a*), (*b*)] report on the speciation of the hydrous iron and manganese oxide phases, and especially the transformations that these materials undergo upon mixing of riverine waters with surface waters of the eastern Caribbean. They report measurements of the photoreductive dissolution of hydrous Mn oxide phases, its dependence on both the organic carbon content of these waters and the influence of light on the overall process.

A study which also concentrates on processes occurring at the riverine-seawater transition is that of *Moore and Todd* [this issue] who used $^{228}Ra/^{226}Ra$ and $^{224}Ra/^{228}Ra$ isotopic ratios to trace the Orinoco plume in the Eastern Caribbean. Their results allowed identification of waters from the Amazon admixed with the Orinoco estuarine water. The radium isotope data also yielded insight into sedimentary mixing dynamics in the region of the Orinoco mouth. The complexity of oceanic processes occurring near the mouths of large rivers is currently under study [see *Nittrouer et al.*, 1991].

If the knowledge gained by the study of a photochemical system is to be of interest to other than photochemists, it remains to be integrated into other oceanographic problems. Earlier we mentioned the potential use of photochemically produced transients and metastable species as water mass tracers and indicators [e.g. *Schott et al.*, 1988]. A paper by *Sikorski and Zika* [this issue] attempts to combine a physical oceanographic model of mixed-layer dynamics with what is known chemically of one of the better studied photochemical systems in seawater, namely, the photoproduction of hydrogen peroxide. The goal of such studies is to see whether a reasonable prediction of the observed hydrogen peroxide distribution can be obtained.

5. CONCLUSIONS AND SOME FUTURE PROJECTIONS

Over a century ago, a report in *Nature* [*Caldwell*, 1890] commented on the occurrence of (freshwater) alligators and crocodiles, observed at both Barbados and aboard a log in the Gulf of Paria and speculated upon their riverine sources. Only a decade ago, an oceanographic cruise to measure the concentration of photochemically produced transients such as the superoxide radical and hydrogen peroxide in the mid-Caribbean and their relationship to riverine sources would have appeared equally novel. The results reported in this section show that it is now feasible to observe large scale (~1000 km) seasonal variations in surface water photoreactivity over much of the eastern Caribbean basin and that this photoreactivity results principally from seasonally varying riverine inputs of organic chromophores and nutrients. Smaller scale (10-100 km) studies in the Orinoco delta and Gulf of Paria showed that estuarine processes do not effect major net removal of colored organic matter. Hence riverine chromophore inputs play a dominant role in open-water photochemistry, rather than being limited, by estuarine removal, to the nearshore region. These studies also clarified details of the mechanisms and the fluxes of the oceanic H_2O_2 cycle. For example, measured superoxide production rates appear to be consistent with the observed H_2O_2 photoproduction rates, as has been previously hypothesized. Wavelength dependent H_2O_2 production rates as well as light and dark loss rates measured are essential for modelling the H_2O_2

distribution in terms of its sources, sinks, and behavior in the surface mixed layer.

The current focus on the effects of increased surface ultraviolet radiation from depletion of stratospheric ozone on biochemical and geochemical processes underlines the relevance of understanding photochemical transformations in the ocean. The coupling of photoprocesses to the oceanic Fe, Cu and Mn cycles is another area in which current research trends indicate a convergence of photochemistry and ocean biogeochemistry. The increasing use of remote sensing platforms for the broad scale synoptic and dynamic description of oceanic processes leads to the need to understand the optical properties of the oceans and atmosphere. There is a particular need to be able to use these platforms in understanding processes occurring in the continental margins. In these contexts, the extension of chemical descriptions of the oceans to include the photooxidizing and photoredox capacity of a range of reactive transients such as the exited states of DOM chromophores, singlet oxygen, solvated electrons, hydroxyl radicals, superoxide anion, carbon centered radicals, hydrogen peroxide and the metastable oxidation states of transition metals is an ongoing challenge.

Acknowledgments. We would like to thank Captain R. Morgan and the crew of the R/V Columbus Iselin for their support in the field. We especially thank the late Julio Perez, Director of the Instituto Oceanografico de Venezuela at Cumana, for crucial logistical assistance, and Jaime Bonilla and his colleagues of that institute for their close collaboration. We thank our anonymous reviewers also. This work would not have been possible without the continued support of the Office of Naval Research and the National Science Foundation.

REFERENCES

Amador, J.A., P. J. Milne, C.A. Moore, and R.G. Zika, Extraction of chromophoric humic substances from seawater, *Mar. Chem.*, 29, 1-17, 1990.

Bidigare, R.R., M.E. Ondrusek, and J.M. Brooks, Influenece of the Orinoco River outflow on distributions of algal pigments in the Caribbean Sea, *J. Geophys. Res.*, this issue.

Blough, N.V., and R.G. Zepp (eds.), Effects of solar radiation on biogeochemical dynamics in aquatic environments, *Tech. Rep., WHOI-90-09*, Woods Hole Oceanogr. Inst., Woods Hole, Mass, 1990.

Blough, N.V., O.C. Zafiriou and J. Bonilla, Optical absorption spectra of waters from the Orinoco River outflow: Terrestrial input of colored organic matter to the Caribbean, *J. Geophys. Res.*, this issue.

Bonilla, J., W. Senior, J. Bugden, O. Zafiriou, and R. Jones, Seasonal distribution of nutrients and primary productivity on the eastern continental shelf of Venezuela as influenced by the Orinoco River, *J. Geophys. Res.*, this issue.

Busalacchi, A.J. and J. Picaut, Seasonal variability from a model of the tropical Atlantic Ocean, *J. Phys. Oceanogr., 13*, 1564-1588, 1983.

Caldwell, A.L. *Nature*, Sept 11, 1890.(See Then and now, *Nature, 347*, (6289), Sept 13, 1991)

Conrad, R., and W. Seiler, Photooxidative production and microbial consumption of carbon monoxide in seawater. *FEMS Lett., 9*, 61-64, 1980.

Dietrich, G., Uber Bewegung und herkunft des Golfstromwassers, *Veroff. Inst. Meereskde. Berlin. N.F. (A), 33*, 53-91, 1937.

Dister, B., and O.C. Zafiriou, Photochemical free radical production rates in the eastern Caribbean, *J. Geophys. Res.*, this issue.

Etter, P.C., P.J. Lamb, and D.H. Portis, Heat and freshwater budgets of the Caribbean Sea with revised estimates for the central american seas, *J. Phys. Oceanogr., 17*, 1232-1248, 1987.

Farmer, C.T., C.A. Moore, R.G. Zika, and R.J. Sikorski, Effects of low and high Orinoco River flow on the underwater light field of the eastern Caribbean basin, *J. Geophys. Res.*, this issue.

Froehlich, P.N., Jr., D.K. Atwood, and G.S. Giese, Influence of Amazon River discharge on surface salinity and dissolved silicate concentration in the Caribbean Sea, *Deep Sea Res., 25*, 735-744, 1978.

Hebura, G.W., and R.C. Rhodes, Numerical simulation of wind forced seasonal and interannual variability of the transport through the Caribbean Sea. *EOS Trans. AGU, 68*, 337, 1987.

Johns, W.E., T.N. Lee, F.A. Schott, R.J. Zantopp, and R.H. Evans, The north Brazil current retroflection: seasonal structure and eddy variability. *J. Geophys. Res., 95*, 22,103-22,120, 1990.

Jones, R.D., and J.A. Amador, Methane and carbon monoxide production, oxidation and turnover times in the Caribbean Sea as influenced by the Orinoco River, *J. Geophys. Res.*, this issue.

Kieber, D.J., J. McDaniel, and K. Mopper, Photochemical source of biological substrates in seawater: implications for carbon cycling, *Nature, 341*, 637-639, 1989.

Kinder, T.H., G.W. Heburn, and A.W. Green, Some aspects of the Caribbean circulation, *Mar. Geol., 68*, 25-52, 1985.

Lewis, W.M., Jr., and J.F. Saunders III, Concentration and transport of dissolved and suspended substances in the Orinoco River, *Biogeochemistry, 7*, 203-240, 1989.

Mazeika, P.A., D.A. Burns, and T.H. Kinder, Mesoscale circulation east of the southern Lesser Antilles, *J. Geophys. Res., 85*, 2743-2758, 1980.

Micinski, E., L.A. Ball, and O.C. Zafiriou, Photochemical oxygen activation: Superoxide radical detection and production rates in the eastern Caribbean, *J. Geophys. Res.*, this issue.

Miller, S., Photochemistry of natural water systems, *Environ. Sci. Technol., 17*, 568A-570A, 1983.

Moffet, J.W., and O.C. Zafiriou, Photochemical decomposition of hydrogen peroxide in surface waters of the eastern Caribbean and Orinoco River, *J. Geophys. Res.*, this issue.

Moffett, J.W., and R.G. Zika, Photochemistry of copper complexes in seawater, in *Photochemistry of environmental aquatic systems* edited by R.G. Zika and W.J. Cooper, *ACS Symp. ser., 327*, Chap 9, American Chemical Society, Washington, D.C 1987.

Molinari, R.L., D.K. Atwood, C. Duckett, M. Spillane, and I. Brooks, Surface currents in the Caribbean Sea as deducted from satellite tracked drifting buoys. *Proc. Gulf and Caribbean Fisheries Institute*, RSMAS, Univ. of Miami, Coral Gables, pp. 106-113, 1979.

Molinari, R.L., W.D. Wilson, and K. Leaman, Volume and heat transports of the Florida current: April 1982 through August 1983, *Science, 227*, 295-297, 1985.

Moore, C.A., C.T. Farmer, and R.G. Zika, Influence of the Orinoco River on hydrogen peroxide distribution and production in the eastern Caribbean, *J. Geophys. Res.*, this issue.

Moore, W.S., and J.F. Todd, Radium isotopes in the Orinoco estuary and eastern Caribbean Sea, *J. Geophys. Res.*, this issue.

Moore, W.S., J.L. Sarmiento, and R.M. Key, Tracing the Amazon component of surface Atlantic water using ^{228}Ra, salinity, and silica, *J. Geophys. Res., 91*, 2574-2580, 1986.

Mopper, K., X. Zhou, R.J. Kieber, D.J. Kieber, R.J. Sikorski, and R.D. Jones, Photochemical degradation of dissolved organic carbon and its impact on the oceanic carbon cycle, *Nature, 353*, 60-62, 1991.

Morrison, J.M., and W.D. Nowlin, Jr., General distributions of water masses within the eastern Caribbean Sea during the winter of 1972 and fall of 1983, *J. Geophys. Res.*, 87, 4207-4229, 1982.

Muller-Karger, F.E., C.R. McClain, and P.L. Richardson, The dispersal of the Amazon's water. *Nature, 333*, 56-59, 1988.

Muller-Karger, F.E., C.R. McClain, T.R. Fisher, W.E. Esaias, and R. Varela, Pigment distribution in the Caribbean Sea: Observations from space. *Prog. Oceanogr., 23*, 23-64, 1989.

Newman, L. (Ed.), *Gas Liquid Chemistry of Natural Waters*, vols 1 and 2, Brookhaven National Laboratory, Upton, N.Y., (Avail as NTIS BNL51757 from Natl. Tech. Inf. Serv., Springfield, Va), 1984.

Nittrouer, C.A., D. J. DeMaster, A.G. Figueiredo, and J.M. Rine, AmasSeds: An interdisciplinary investigation of a complex coastal environment, *Oceanography, 4 (1)*, 3-7, 1991.

Nof, D., and D.B. Olson, On the flow through broad gaps with application to the Windward Passage *J. Phys. Oceanogr. 13*, 1940-1956, 1983.

Redden, G.D., Characteristics of photochemical production of carbon monoxide in seawater. M.Sc. thesis, Oregon State Univ., Corvallis, 1983

Richardson, P.L., and T.K. McKee, Average seasonal variation of the Atlantic equatorial currents from historical ship drifts. *J. Phys. Oceanogr. 14*, 1226-1238, 1984.

Samuels, G., A shipboard data acquisition, logging and display system, Proc. Oceans '88, pp 648-650, Instit. of Elec. and Electron. Eng., New York, 1988.

Schott, F., K.D.Leaman, and R.G. Zika, Deep mixing in the Gulf of Lions, revisited, *Geophys. Res. Lett., 15*, 800-803, 1988.

Sholkovitz, E.R., Flocculation of dissolved organic and inorganic matter during the mixing of river water and seawater, *Geochim. Cosmochim. Acta, 40*, 831-845, 1976.

Sholkovitz, E.R., E.A. Boyle, and N.B. Price, The removal of dissolved humic acids and iron during estuarine mixing. *Earth Planet. Sci. Lett., 40*, 130-136, 1978.

Sikorski, R.J., and R.G. Zika, Modeling mixed-layer photochemistry of H_2O_2: Optical and chemical modeling of production, *J. Geophys. Res.*, this issue.

Stalcup, M.G., and W.G. Metcalf, Current measurements in the passages of the Lesser Antilles. *J. Geophys. Res.*, *77*, 1032-1049, 1972.

Sturges, W., Observations of deep-water renewal in the Caribbean Sea. *J. Geophys. Res.*, *75*, 7602-7610, 1970.

Waite, T.D., and R. Szymczak, Manganese dynamics in surface waters of the eastern Caribbean, *J. Geophys. Res.*, this issue (*a*).

Waite, T.D., and R. Szymczak, Particulate iron formation dynamics in surface waters of the eastern Caribbean, *J. Geophys. Res.*, this issue (*b*).

Wilson, D.F., J.W. Swinnerton, and R.A. Lamontagne, Production of carbon monoxide and gaseous hydrocarbons in seawater: relation to dissolved organic carbon, *Science*, *168*, 1577-1579, 1970.

Worthington, L.V., Recent oceanographic measurements in the Caribbean Sea. *Deep Sea Res.*, *13*, 731-739, 1971.

Wust, G., On the stratification and the circulation in the cold water sphere of the Antillean-Caribbean basins, *Deep Sea Res.*, *10*, 165-187, 1963.

Zafiriou, O.C., Natural water photochemistry, in *Chemical Oceanography*, vol. 8, 2nd ed., edited by J.P. Riley and R. Chester, pp. 339-379, Academic, San Diego, Calif., 1983.

Zafiriou, O.C., J. Joussot-Dubien, R.G. Zepp, and R.G. Zika, Photochemistry of natural waters, *Environ. Sci. Technol.*, *18*, 358A-371A, 1984.

Zhou, X., and K. Mopper, Carbonyl compounds in the lower marine troposphere over the Caribbean Sea and Bahamas, *J. Geophys. Res.*, this issue.

Zika, R.G., Advances in marine photochemistry 1983-1987. *Rev. Geophys.*, 25, 1390-1394, 1987.

Zika, R.G., and W.J. Cooper (eds.), *Photochemistry of Environmental Aquatic Systems, ACS Symposium Series, 327*, American Chemical Society, Washington, D.C., 1987.

Zika, R.G., and E.S.Saltzman, Interaction of ozone and hydrogen peroxide in water: implications for analysis of H_2O_2 in air, *Geophys. Res. Lett.*, *9*, 231-234, 1982.

P.J. Milne and R.G.Zika, Rosenstiel School of Marine and Atmospheric Science, University of Miami, 4600 Rickenbacker Causeway, Miami, FL 33149-1098.

O.C. Zafiriou, Woods Hole Oceanographic Institution, Woods Hole, MA 02543.

(Received November 20, 1991;
revised August 28, 1992;
accepted September 11, 1992.)